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An Investigation of the Role of
Recycled Black Liquor in Sulfate Pulping

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AN INVESTIGATION OF THE ROLE OF RECYCLED BLACK LIQUOR IN SULFATE PULPING

A thesis submitted by

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INTRODUCTION

In sulfate pulping operations black liquor is widely used instead of fresh water to dilute the strong white liquor charged to a digester. This practice increases the solids content of the spent liquor and thereby reduces the amount of evaporation required in the alkali recovery system. Since the recycled black liquor commonly constitutes from 20 to 50% of the total liquor volume, an appreciable quantity of reaction products from previous cooks and possibly a significant amount of residual cooking chemicals are introduced at the beginning of a cook. This study is an effort to gain some understanding of the role which the components of this recycled liquor have in the pulping process.

Previous investigations into the effects of recycled black liquor have been, for the most part, experimental pulping studies in which the amount of recycled black liquor has been varied and resulting changes in pulp properties followed. These studies have been made with single black liquors taken from commercial pulping operations, and they have been made both with the white liquor chemical charge held constant and with it varied to compensate for the residual alkali in the recycled liquor. The findings of these investigations have been contradictory and have not resulted in the establishment of any general conclusions regarding either how the pulp is affected or what black liquor properties determine these effects.

In a series of experimental cooks on balsam and on hemlock, Crandall and Enderlein (1) found that when the amount of recycled black

liquor was increased, the yields and permanganate numbers of the resulting pulps indicated that the recycled liquor had a greater cooking effect then would be expected from its residual alkali content. Hart and Strapp (2) made a similar investigation with spruce and found the yields and permanganate numbers indicated that the recycled liquor did not have a cooking effect commensurate with the amount of residual alkali it contained.

The effects of recycled black liquor on sulfate pulps have been considered in other investigations (3-13) made using a variety of pulping conditions, a number of pulpwoods, and various analytical methods to estimate the residual chemicals in the black liquors. A review of the findings of these studies suggests that the pulping process may be influenced by the recycled liquor in a number of ways, and that it might be useful to investigate more explicitly the manner in which the various properties of the recycled liquor affect the pulping reactions.

Present information regarding the variables in sulfate pulping and the composition of black liquor indicates that the pulping process might be expected to be affected by the recycled black liquor for a number of reasons.

a. The organic components of the recycled black liquor could undergo further degradation and in so doing consume additional quantities of the pulping chemicals.

b. A black liquor might contain alkali in a form which could be utilized in the pulping reactions of a subsequent cook. Analytical

methods which are available for determining alkali in black liquor are empirical procedures, and the actual cooking value of the alkali indicated by them has not been established.

c. The pulping reactions might be significantly affected by the sulfide content of the recycled liquor. Since black liquors usually contain appreciable amounts of sodium sulfide, the recycled liquor could bring about a rather large increase in the sulfidity of the cooking liquor.

d. The organic materials in the recycled black liquor might exert an effect not involving the further degradation of these residues. Lusby and Maass (14) have found that the rate of alkaline delignification of wood is decreased by the presence of organic reaction products in the cooking liquor. These workers suggested that the decrease resulted from an adsorption of alkali by the organic materials. Theories involving catalytic (13) and buffering actions (5, 7) of these materials have also been offered as explanations of the effect of recycled liquor on various pulp properties.

The ultimate objective of this investigation is to provide a better understanding of the manner in which recycled black liquor affects the sulfate pulping process. The approach used in seeking this objective was to consider the four effects listed above and to determine if these effects were actually involved in the pulping situation studied. The pulping of jack pine (Pinus banksiana) was considered using conditions which gave yields of approximately 45%.

In the initial phase of the work a determination was made of the degree to which the organic materials in a black liquor were degraded by recooking. This information was sought because it would provide an indication of any appreciable consumption of white liquor chemicals by the recycled black liquor. The value of a direct analytical measurement of chemical consumption would be questionable because of the uncertainties inherent in the available methods.

The degradation occurring on recooking a black liquor with fresh white liquor but without additional wood was considered in evaluating the stability of these organic residues. By this procedure the black liquor was recooked under more severe conditions than would have been encountered if wood had been present and had been consuming chemical. The changes occurring under these conditions were regarded, therefore, as an indication of the maximum extent to which the materials would be altered during actual recooking in the presence of wood. This assumption is supported by Kimble's (15) findings that isolated thiolignin is more severely degraded on recooking with white liquor than on recooking with white liquor and wood.

The results of the initial work, which indicated that the organic components of black liquor are relatively unaffected by recooking, made it convenient to employ a three factor factorial design experiment to determine if a recycled liquor does affect the pulping process because of its residual alkali, residual sulfide, or organic material. The factorial design procedure is a method of experimentation in which the effects of a number of factors are studied simultaneously and the

statistical technique of analysis of variance is employed to estimate the relative effect attributable to each of the factors (16, 17).

There are a number of aspects of the factorial arrangement which make it especially suited to the present problem. The problem involves determining whether a complex process is affected by three variables, and it necessitates ascertaining this in the presence of irrelevant variation which could obscure the effects of the variables being studied. In addition to being adapted to a statistical procedure for setting the risk at which conclusions are drawn, the factorial design offers several advantages over a more conventional design in which each factor would be considered individually.

a. The factorial design is more efficient than the conventional design. With the same number of experiments it is possible to consider more than one variable without any sacrifice of precision.

b. Possible interactions between variables are indicated in a factorial design experiment.

c. Since a number of factors are varied simultaneously, the conclusions of a factorial design experiment are less influenced by arbitrary limitations than are those of a conventional design experiment.

PRESENTATION OF THE PROBLEM

The purpose of this investigation is to obtain a better understanding of the role of recycled black liquor in the sulfate pulping process. In the experimental program the following questions have been considered because their answers would contribute to that understanding.

Do the organic components of a black liquor undergo any further degradative changes as the liquor is recooked?

Is a sulfate cook of the type being considered appreciably affected by the residual alkali, residual sulfide, or organic material in the recycled black liquor?

EXPERIMENTAL PROCEDURES

GENERAL

WOOD PREPARATION

The investigation was made with a sample of seasoned jack pine taken from a pulpmill woodyard. Three eight-foot sticks were selected, the bark removed, sample disks cut, and half-inch chips prepared with a Carthage semicommercial chipper. The chips were screened on a 0.25-inch wire screen and hand sorted to remove knots, slivers, and oversize pieces. The accepted chips were weighed into plastic bags, and stored at 9°C. until used. The following conventional analytical procedures were used to obtain a physical and chemical characterization of the wood. The results are given in Table XXXV of the Appendix.

The wood species was confirmed according to TAPPI Suggested Method T 8 sm-40. The moisture content of the chips and the specific gravities of sample disks were determined using TAPPI Standard T 18 m-50.

Institute Method 2 was followed in sampling and preparing the wood for chemical analyses. Sawdust sieved through a 40- and retained by a 60-mesh screen was used in the alpha-cellulose determination. Sawdust passing through a 40-mesh screen was used in the other analyses.

The lignin content was determined by Institute Method 13 on a sample of the wood which had been pre-extracted with alcohol-benzene. The material removed in the pre-extraction was recovered according to Institute Method 11 for extractives.

Pentosans were determined using Institute Methods 23 and 424, respectively, to distill and measure the furfural. Alpha-cellulose was determined according to Institute Method 421 on a sample of the wood which had been pre-extracted with ethanol and then chlorited according to Institute Method 28.

PULPING METHODS

The experimental cooks were made in a four-liter stainless steel autoclave which was heated by immersion in a wax bath. At the completion of a cook the autoclave was removed from the molten wax, the pressure relieved over approximately a fifteen-minute period, and the contents of the autoclave dumped.

After being washed on a cloth drain-box, the cooked chips were mixed with water and defibered by a ten-minute treatment with a British disintegrator. The pulp was screened on a 9-cut laboratory flat screen and the accepted portion air dried.

Concentrated solutions of reagent grade chemicals and boiled distilled water were used to prepare the white liquors for the cooks. The strength of the sodium hydroxide solution was determined by an acidimetric titration to the methyl orange end point. The sodium sulfide solution was standardized using a precipitation titration with ammoniacal silver nitrate (Institute Method 107). The cooking schedule listed in Table I was used throughout the investigation; the white liquor charge was varied slightly so that pulp yields in the 45 to 48% range would be obtained in both phases of the study.

TABLE I

EXPERIMENTAL PULPING CONDITIONS

Liquor - wood ratio, ml./g.	5 1/2/1
Maximum temperature, °C. (Pressure relieved at 100°C.)	173
Time to maximum temperature, hr.	2
Time at maximum temperature, hr.	2

Throughout this investigation the concentrations of chemicals in the white and black liquors have been expressed with the following terms:

Active alkali	$NaOH + Na_2S$ (As NaOH),
Effective Alkali	$NaOH + 1/2Na_2S$ (as NaOH),
Sulfidity	Na_2S/ $NaOH + Na_2S$ (all as NaOH).

PULP ANALYSES

Portions of the airdry screened pulps were ground in a Wiley mill (intermediate model) and analyzed according to Institute procedures. Total yields were calculated by combining the ovendry weights of the screenings and the accepted stock.

Pulp Analysis Procedures

Ovendry content of pulp	Institute Method 423
Alpha-cellulose	Institute Method 421
Lignin (half specified sample size)	Institute Method 428
Permanganate number	Institute Method 410

BLACK LIQUOR ANALYSES

The residual chemicals in the black liquors were estimated by determining effective alkali contents according to TAPPI Standard T 625 m-48 (potentiometric titration to pH 8.3 after treatment with

barium chloride), and sulfide contents using a potentiometric titration with silver nitrate and a silver-silver sulfide electrode (18, 19). The organic solids in the black liquors were calculated from the determinations of total solids and sulfated ash made according to Institute Method 109.

Black liquors prepared in the various cooks and later used for recycling or for analytical evaluation were stored at 9°C. in completely filled bottles.

EFFECT OF RECOOKING ON BLACK LIQUOR COMPONENTS

INTRODUCTION

In order to determine the effect of recooking on its organic constituents, a black liquor prepared in a cook of white liquor and chips only was recooked twice with fresh portions of white liquor but in the absence of wood. The initial black liquor and the two recooked liquors were studied by a series of analytical operations which separated and characterized various fractions of the black liquor components.

Our present knowledge of the chemistry of the sulfate pulping process and of the reaction products found in the black liquor is limited; several reviews on this subject have appeared recently (20-22). In this investigation the purpose of the fractionation procedures was to indicate the extent and nature of changes which occur in the organic components of a black liquor as it is recooked. These constituents have been considered only in terms of analytically separable fractions, and no attempts have been made to isolate or identify specific compounds

occurring in the black liquors. The procedures used were in part conventional analytical methods and in part adaptations of methods used by other workers in other applications. The analytical scheme employed is based upon the separations indicated in Figure 1.

EXPERIMENTAL COOKS

In the cook of wood and white liquor a chemical charge of 18% active alkali and 25% sulfidity was used. Strong black liquor formed in that cook was mixed with fresh white liquor and recooked in the absence of wood. The same cooking schedule and white liquor chemical concentrations were used in the second cook, and the amount of black liquor recooked constituted 25% of the total liquor volume. In the third cook the black liquor was recooked a second time with fresh white liquor. The same amount of additional white liquor chemical per unit volume of black liquor was added; the concentration of the strong white liquor was such that this involved a 31.2% increase in the total liquor volume. The pulping conditions for these cooks are given in Table II.

In the cook with wood, the black liquor was separated from the chips by a series of vacuum filtrations and washings. The pulp was placed on a stainless steel 60-mesh screen set in a large Buchner funnel and was covered with a piece of rubber dental dam. The pulp was sucked dry, suspended in distilled water, allowed to soak for fifteen minutes, and refiltered. Four such washings and filtrations were made. The volumes and the solids contents of the filtrates removed in each step were determined. The solids contents were obtained by evaporating an aliquot of each liquor and drying it at 105°C. for 18 hours.

Figure 1

SEPARATION OF BLACK LIQUOR COMPONENTS

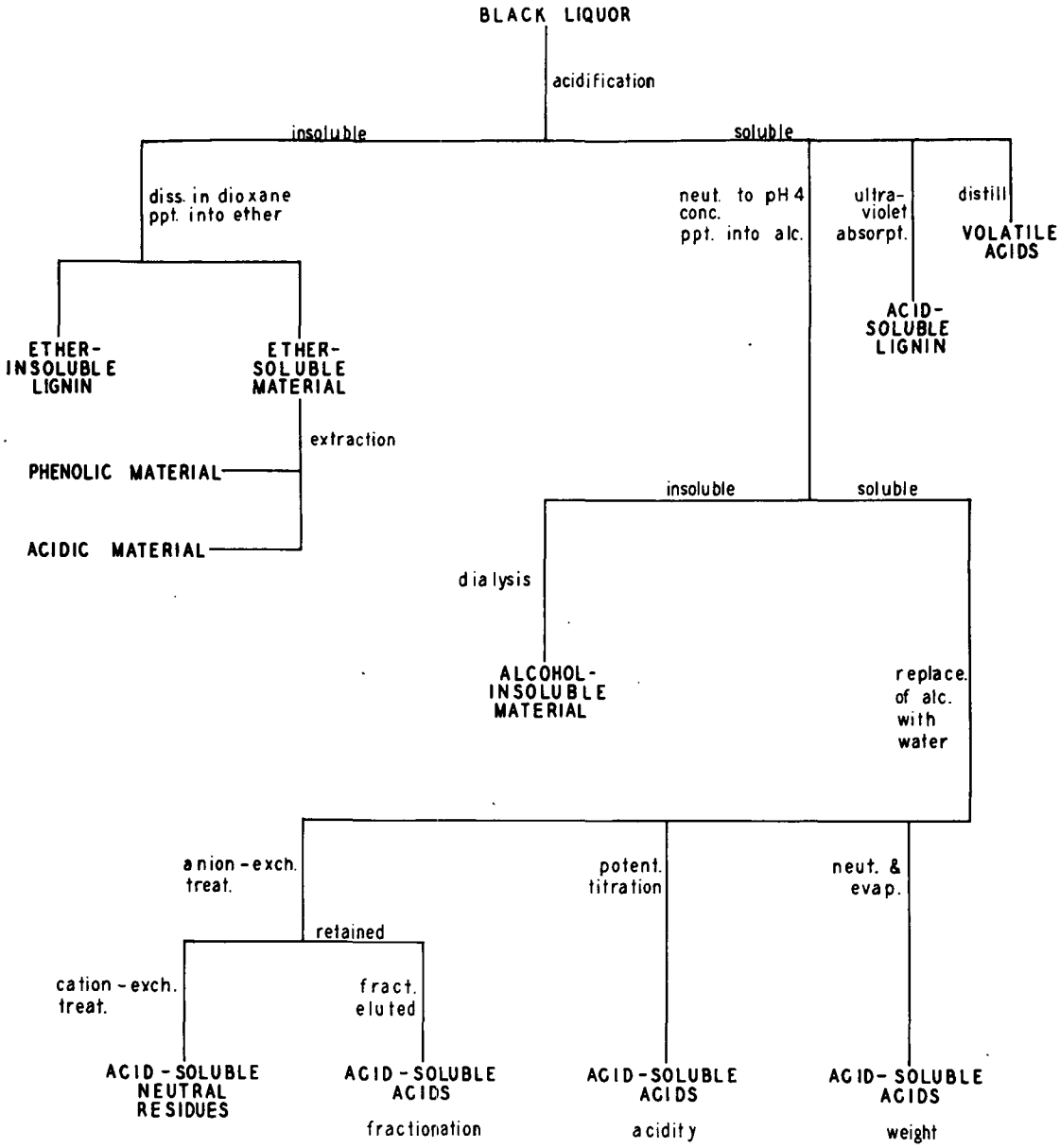

TABLE II

RECOOKING BLACK LIQUOR
COOKING CONDITIONS

Cook	A	B	C
Wood, g. ovendry	451.5	none	none
Recycled black liquor, ml.	none	828	1460
Total liquor volume, ml.	2483	2483	1916
White liquor			
Active alkali, % on wood	18	--	--
Sulfidity, %	25	25	25
Sodium hydroxide, g.	60.95	60.95	38.88
Sodium sulfide, g. as NaOH	20.32	20.32	12.96
Maximum temperature, °C.	173	173	173
Time to maximum temperature, hr.	2	2	2
Time at maximum temperature, hr.	2	2	2

Knowing the total solids contents and the volumes of the solutions it was possible to calculate the proportion of the total dissolved solids which was recovered in the undiluted black liquor drained from the cooked chips. With this information the total volume of strong black liquor resulting from the cook could be estimated, and the results of the various black liquor analyses could be expressed in terms of the total amount of material involved. Preliminary tests on a duplicate cook indicated that the distributions of residual effective alkali and of total solids between the various filtrates were similar. The results of this preliminary work are given in Table III where the residual effective alkali and the total black liquor solids removed in the initial draining and in the first three washings are listed as percentages of the total amounts of these materials recovered in all four solutions.

TABLE III

PULP WASHING TESTS

	Distribution, %	
	Residual Effective Alkali	Black Liquor Total Solids
Strong liquor	69.6	71.5
Wash liquor 1	19.4	20.9
2	7.1	5.5
3	3.9	2.1
	100.0	100.0

The residual effective alkali and sulfide contents of the three black liquors were determined by titration. A comparison of the chemical concentrations in the black liquor with that in the white and recycled black liquors gives an indication of the chemical consumed during a cook. Uncertainties as to the exact significance of analytically determined values for residual chemicals in black liquor prevent the use of these results as conclusive indications of chemical consumption. The results are useful as corroborative evidence.

The determinations of residual chemical were made within several hours of the completion of a cook. Because of the possibility of changes in these materials before the black liquors could be recooked, additional determinations for both effective alkali and sulfide were made on aliquots of the mixed white and recycled black liquors taken at the start of the recooks.

BLACK LIQUOR EVALUATION

Acidification

Precipitation of the acid-insoluble materials was effected by adding a measured volume of black liquor to a 250-ml. centrifuge jar containing dilute sulfuric acid. In the first cook 25-ml. samples of black liquor were added to 150-ml. portions of 3.3% acid; for the other two cooks 75-ml. portions of liquor and stronger acid solutions were used. In each case sufficient acid was used to insure a final pH of approximately 1.5.

After standing overnight, the precipitated material was separated by centrifuging for one-half hour at 2000 r.p.m. The precipitate was washed with and centrifuged from three 200-ml. portions of distilled water. The precipitate was allowed to stand in the final wash water overnight. The original supernatant liquor and three wash solutions were poured off through filter paper, combined, and kept at 9°C. until used in subsequent analyses.

Lignin Purification

The moist acid-insoluble precipitate was dissolved in approximately 100 ml. of dry, purified dioxane (23). A small amount of material did not dissolve and appeared to consist primarily of free sulfur. The dioxane solutions from two duplicate acidification batches (i.e., for Cook A from a total of 50 ml. black liquor) were combined, filtered through a small circle of medium filter paper and distilled under

reduced pressure (water aspirator) to remove the water. After adding several volumes of fresh dry dioxane the solution was concentrated to about 50 ml.

A purified thiolignin was isolated by pouring 6-ml. portions of this dioxane solution into 240-ml. portions of absolute ethyl ether. The procedure used was that described by Brauns (23) and included washing the resulting precipitate with benzene and petroleum ether. The ether-dioxane (40:1) solutions were combined and put aside for subsequent work.

The isolated lignin was dried to a constant weight at 105°C. and the yield reported as other-insoluble lignin. Some characterization of this material was obtained by determining its methoxyl content (Institute Method 18) and its insolubility during an eight-hour Soxhlet extraction with absolute ethanol.

Separation of Ether-Soluble Materials

The solution of ether-dioxane (40:1) soluble, acid-insoluble constituents was evaporated to less than a liter and diluted to one liter with ether. Since this fraction includes phenolic degradation products of lignin, the resin and fatty acids, and certain neutral components of the wood, a separation of this solution into these three groups of material was sought.

First attempts were made to extract the ether solution successively with aqueous solutions of sodium bicarbonate and sodium hydroxide, to acidify the aqueous extracts, and to recover the precipitated material.

When filtration of these precipitates proved impractical, their re-extraction with an ether-dioxane (40:1) mixture was tried and also found to be ineffective.

An indirect procedure was adopted which involved determining the total dissolved material in one aliquot, extracting a second aliquot with bicarbonate and determining the remaining ether-soluble material, and similarly extracting a third aliquot with caustic. By this means it was possible to estimate by difference the amount of acidic, phenolic, and neutral materials present in the ether-dioxane solution.

The procedure used was to extract one 200-ml. aliquot of the ether solution with three 200-ml. portions of 0.1 M sodium bicarbonate and a second 200-ml. aliquot with three 200-ml. portions of 0.1 N sodium hydroxide. After washing each extracted ethereal solution with two portions of distilled water, the solutions were evaporated and the residues were dried under vacuum at 60°C. for one hour. The total dissolved material in the unextracted ether solution was determined by evaporating a 50-ml. aliquot and drying the residue in the same manner.

Estimation of Volatile Acids

After standing for approximately five days at 9°C., the acid-soluble solution, separated during the acidification step, was filtered to remove the sulfur which had precipitated. Aliquots of this filtrate were used in the determination of the volatile acid content of black liquor.

Since a preliminary experiment indicated that volatile acids were still distilled from this filtrate at a practically undiminished rate even as the solution approached dryness, a procedure was adopted in which water was repeatedly added to maintain a fixed volume and a number of successive distillate samples were collected and titrated. This is an empirical method and appreciable amounts of acids were still being evolved when the distillation was stopped. The results, therefore, have comparative but not absolute value.

The determination was carried out in a 250 ml. distilling flask which was provided with a separatory funnel and a water-cooled condenser. An 100-ml. sample of the acid-soluble solution was used and a volume of between 75 and 125 ml. was maintained by adding the necessary distilled water through the separatory funnel. Five 100-ml. samples of distillate were collected and titrated to the phenolphthalein end point with 0.1 N sodium hydroxide. A distillation rate of approximately 100 ml. in 30 minutes was used. Qualitative tests for sulfate ion in the condensates were negative.

The acidities of the five fractions were totalled and reported both as milliequivalents of volatile acids and as grams of volatile acids calculated as acetic acid.

Determination of Soluble Lignin

A measure of the amount of lignin not precipitated on acidification was obtained from the ultraviolet absorption of the solution of acid-soluble material. These measurements were made with a Beckman

Spectrophotometer. The solutions from the three cooks were diluted so that the concentrations of the three samples, respectively, were equivalent to 3.75, 7.50, and 11.25 ml. black liquor per liter.

Some uncertainty is introduced into this procedure by the ultraviolet absorption of certain furan materials which apparently are of carbohydrate origin (24). This uncertainty is at a minimum in this work because: (a) a coniferous wood (low pentosan content) is being considered, (b) the material has not been heated under acid conditions, and (c) a relatively large amount of lignin is being determined. As a precaution, however, the lignin content was determined at both the conventionally used wavelength of 280 mmu and the lower wavelength of 220 mmu where the absorption of lignin is high but that of most carbohydrate materials is low.

The lignin content was calculated from the measured absorbance by the following formula: $c = A/ab$, where A = absorbance (optical density), a = absorptivity (specific extinction), b = cell length in cm., and c = concentration in g./l. The absorptivities used were 48 and 18 at wavelengths 220 and 280 mmu as have been reported for a spruce native lignin by Barton (25). The similarity between the absorption curves for these samples and for native lignin, and the close agreement between the lignin values found at the two wavelengths suggest that this procedure gives a good estimate of the acid-soluble lignin.

Examination of the Polysaccharidic Material

Another portion of the filtered acid-soluble solution was titrated potentiometrically with sodium hydroxide solution to a pH of 4.0 so as to neutralize most of the excess sulfuric acid. This solution was concentrated from several liters to several hundred ml. under reduced pressure (at 55°C.) in a circulating evaporator similar to that described by Mitchell, Shildneck, and Dustin (26). The concentrated solution was poured into four volumes of absolute ethanol, and the resulting precipitate was separated on a sintered glass funnel. The filtrate was again concentrated, poured into more ethanol, and filtered.

After drying the precipitate to remove the remaining ethanol, the material was dissolved in about 500-ml. water. The major portion of the sodium sulfate was removed from the solution by dialyzing it against running tap water for 23 hours in a "Visking" cellulose sausage casing (high stretch). A preliminary trial indicated that the carbohydrate material contained in this solution did not pass through the "Visking" membrane. In this trial a portion of the solution was dialyzed batchwise against distilled water for a twelve-hour period. The original solution gave a positive alpha-naphthol test for carbohydrates (Molich test) but the solution outside the "Visking" sack did not.

The dialyzed solution was diluted to one liter and divided into two equal portions. One portion was hydrolyzed with 3% sulfuric acid for 12 hours on a steam bath and then boiled briskly for 10 minutes, cooled, and rediluted to 500-ml. The hydrolyzed and nonhydrolyzed

samples were both treated with an excess of barium carbonate, mixed with Celite (a diatomaceous earth material), and filtered through a sintered glass funnel containing a layer of purified asbestos fibers.

The reducing values of the solutions were determined using as the reagent an alkaline solution of cupric sulfate and sodium potassium tartrate (Somogyi's sugar reagent). This determination is performed by heating the sample solution and the reagent in boiling water for a 40-minute period and titrating the reduced copper iodometrically.

The Somogyi reagent was prepared and used in the usual manner except that the suggested modification of including the potassium iodate in the original reagent was followed (27). In making these tests 5-ml. volumes of both the reagent and the sample solutions were used. This volume of solution was equivalent, in the samples from the three cooks, to 0.25, 0.75, and 0.75-ml. of black liquor.

The reducing value is proportional to the difference between the volumes of thiosulfate used in a blank and in the test determinations. In order to express the results in terms of the reducing power of glucose, the reagent was standardized against known volumes of a standard glucose solution.

A consideration of the source and previous treatment of this fraction suggested that the reducing value found indicated the presence of polysaccaridic material. The appreciable reducing values of the hydrolyzed samples and negligible reducing values of the nonhydrolyzed samples supported this view. As further support, paper partition

chromatograms were prepared to identify sugars present in the hydrolyzates, and ultraviolet absorption curves were prepared to detect and estimate possible traces of ligneous materials in these solutions.

To prepare the chromatograms the filtered, barium carbonate-treated, hydrolyzate was passed through a cation-exchange column (Ionac C-200, hydrogen form) and concentrated under reduced pressure to a thick sirup. This sirup was compared to a "known" sirup made up of the following sugars: xylotriose, xylobiose, galactose, glucose, mannose, arabinose, xylose, and rhamnose.

Chromatograms were prepared on 4 by 24-inch strips of Whatman No. 1 filter paper using pyridine as the developer and a 48-hour development, and using an ethyl acetate-acetic acid-water (9:2:2) mixture and a 24-hour development. The dried chromatograms were sprayed with an aniline hydrogen phthalate solution which was prepared by dissolving 1.66 g. phthalic acid anhydride and 0.93 g. aniline in 100-ml. of butanol saturated with water (28).

The ultraviolet absorption was measured on a portion of the dialyzed, nonhydrolyzed solution. For the three cooks the concentrations of this solution were equivalent to 50, 150, and 150-ml. of black liquor per liter.

Evaluation of the Acid-Soluble Acids

The alcoholic solution of the acid-soluble material was diluted with water and the alcohol distilled off under reduced pressure. This solution was neutralized with a saturated solution of barium hydroxide

and the precipitate removed by filtration through a sintered glass funnel containing a layer of purified asbestos fibers and a layer of Celite. After passing the filtrate and some wash water through an Amberlite IR-120 cation exchanger (hydrogen form), the combined solution was concentrated under reduced pressure and quantitatively diluted to 500-ml.

An 100-ml. aliquot, equivalent in the case of Cook A to 10-ml. of black liquor, was taken and titrated potentiometrically with 0.1 N sodium hydroxide using a standard Beckman pH meter. Readings were made at each half milliliter increment and the titration was continued until a pH greater than 10.5 had been reached. The solution was then boiled for five minutes, allowed to stand for at least five hours, and back-titrated potentiometrically with 0.06 N hydrochloric acid.

The plot of this data gave the three end points indicating the neutralization of the remaining strong acids (pH 3.0), the neutralization of the free organic acids (pH 7.5), and the back-titration neutralization of the excess sodium hydroxide (pH 7.5). From these end points a free organic acidity and a saponification value for the fraction were calculated.

A second 100-ml. aliquot of the barium hydroxide neutralized and exchange resin treated solution was used for a gravimetric determination of the total organic matter in this fraction. The solution was neutralized with the amount of sodium hydroxide indicated by the potentiometric titration. After being evaporated to near dryness, the

sample was dried under reduced pressure at 60°C. to a constant weight. The weight of organic material was calculated by correcting for the sodium sulfate and for the sodium in the organic salts as indicated by the previously described potentiometric titrations.

Since an estimate of the equivalent weight distributions of these acids in the various black liquors would provide an indication of their degradation during recooking, an effort was made to isolate and separate the acids occurring in the nonvolatile, alcohol-soluble, acid-soluble fraction. The technique eventually adopted was to pass the solution through a strongly basic anion exchange column in its carbonate form. After fractionally eluting the retained acids, half of each fraction was titrated to determine the equivalents of acid present and the other half was used to determine the weight of the sodium salts of these acids. The problem of removing the excess elutant from the samples was handled by using a solution of a volatile salt for the elutant as has been suggested by Bryant and Overell (29).

The anion exchange column was 25 mm. in diameter and contained 10 cm. of Amberlite IRA-400 strongly basic exchange resin which had been ball milled and screened to a 50-100 mesh size. The column was used in its carbonate form and was reconditioned between determinations by a wash with sodium hydroxide solution, a water backwash, a wash with sodium carbonate solution, and a final water wash.

A second portion of the aqueous solution of alcohol-soluble and acid-soluble material was used for this fractionation. The 200-ml. aliquots taken were equivalent to 20, 60, and 60-ml. of the three black

liquors. After passing the solution through the column, the resin was rinsed with a liter of water; the combined solution and rinse water were later utilized in the determination of the nonacidic material.

The retained acids were fractionally eluted from the resin with a 5 g./l. solution of ammonium carbonate. Fractions of 50 ml. were removed, diluted to 100 ml. and divided into two equal portions. One portion was boiled for twenty minutes to remove the excess ammonium carbonate. Preliminary work, the results of which are listed in Table IV, indicated that such a boiling period would remove the ammonium carbonate but not seriously affect an organic salt such as ammonium acetate.

After cooling the boiled sample, a displacement titration for ammonium ion was made by adding 1-ml. of neutralized formaldehyde solution (40%), waiting one minute, and titrating with 0.1 N sodium hydroxide to the phenolphthalein end point (30). This titration is based upon the formation of an associated ammonium-formaldehyde complex and it gave an estimate of the total anion concentration of the solution.

The second portion of each fraction was neutralized with the amount of sodium hydroxide indicated by the titration. After evaporation, the residues were dried at 105°C. for thirty minutes. The average equivalent weight of the acids in each fraction was calculated from the weight of the dried residue.

TABLE IV

VOLATILITY OF AMMONIUM SALT SOLUTIONS
(50-ml. samples of solution)

Ammonium Carbonate Boiling Time, min.	NH_4^+ Content, meq.
0	1.70
5	1.17
10	0.25
15	0.047
20	0.022
30	0.000

Ammonium Acetate Boiling Time, min.	NH_4^+ Content, meq.
0	0.383
10	0.379
15	0.377
20	0.375
30	0.367

Determination of Neutral Residues

The solution of the acid-soluble material which was not retained by the Amberlite IRA-400 (carbonate form) anion exchanger was passed through a column of Amberlite IR-120 (hydrogen form) cation exchanger. The resin was washed with water and the combined solutions were concentrated under reduced pressure (at 55°C.) and quantitatively diluted.

Aliquots, equivalent in the cases of the three cooks to 5, 15, and 15-ml. of black liquor, were evaporated to dryness and the residues dried for 30 minutes at 105°C. and weighed.

In an effort to gain some information concerning the nature of this nonacidic black liquor component, the ultraviolet absorptions and

reducing values before and after hydrolysis were determined according to the procedures already described.

EFFECT OF THE PROPERTIES OF RECYCLED BLACK LIQUOR ON PULPING

INTRODUCTION

A factorially designed series of experimental cooks was used to determine in what ways the sulfate pulping process is affected by the residual alkali, organic material, and residual sulfide content of the recycled black liquor. After establishing a fixed cooking procedure and white liquor charge, twenty-four cooks were made in which the properties of the recycled black liquors were varied according to the factorial design shown in Table V. The factors of residual effective alkali, organic material, and residual sulfide were considered at four, three, and two levels, respectively. The effect of these factors on the pulping process was measured in terms of the effect on the total yield, lignin content, alpha-cellulose content, permanganate number, and brightness of the pulp.

ANALYSIS OF VARIANCE

Using each of the above-listed pulp properties as the dependent variable, the statistical method of analysis of variance was applied to determine if the pulping process was significantly affected by any of the three factors. Mathematically, the method involves estimating the variance in the dependent variable, partitioning it according to its sources of origin, and using a null hypothesis technique to determine if the variance attributed to any factor is a real effect or possibly only the result of normal variation.

TABLE V

FACTORIAL ARRANGEMENT OF EXPERIMENTAL COOKS

Residual Sulfide	Organic Material	Residual Effective Alkali			
		a_1	a_2	a_3	a_4
s_1	b_1	1	2	3	4
	b_2	5	6	7	8
	b_3	9	10	11	12
s_2	b_1	13	14	15	16
	b_2	17	18	19	20
	b_3	21	22	23	24

The theory and manipulations of the method are given in detail by standard textbooks (31, 32). The method is based upon the principles (a) that variance is an additive property and (b) that the estimate of variance made on the individuals within groups and the estimate made on the means of the various groups may be compared by a significance test which will indicate the probability that the estimates are equivalent. An important assumption in the use of this technique is that the residual variance, or that variance arising from experimental errors and uncontrolled variables, remains relatively constant throughout the experiment.

The F test, or significance test, used in the analysis of variance indicates only the level of confidence at which a conclusion can be drawn as to whether or not a given variable is affecting the process. It does not measure the magnitude of the effect; it does denote the

consistency or reliability with which the data indicate an effect. If the test indicates that a factor is significant at the one percent level, this means that in the absence of a significant effect the observed values for the dependent variable could have occurred by chance not more than once in a hundred times.

As the textbook discussions point out, the analysis of variance method uses calculations of the mean squares as estimates of variance. Mean squares are unbiased estimates of the averages of the squares of the deviations of individuals about their respective group means, of the group means about the grand mean, etc. The mean squares can be considered to be summations of the various components of variance. Table VI shows how this breakdown is made for the situation under study.* The various components of variance are indicated by the symbol σ^2. To test whether the BxS interaction is real, the null hypothesis is made that it is not. If this is so M_{BS} and M_R are independent estimates of the same quantity. The F test indicates the probability that the null hypothesis is correct and that the observed difference in the two estimates is simply the result of chance variation. The significance of the other components of variance is determined in a similar manner.

The results of the analyses of variance have been reported in the form of a table giving the sources of variance and the mean squares for each dependent variable. The mean squares of the significant effects are marked to denote significances at the 5%, 1%, and 0.1% levels.

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* The convention has been followed of designating factors or sources of variance with capital letters and of designating the various levels of the factors with small letters.

A more complete table which includes the degrees of freedom and the sums of squares is given in Table XXXVIII of the Appendix. In making the F tests the practice of pooling the degrees of freedom and sums of squares of the nonsignificant effects has been followed in order to obtain better estimates of the residual variance. The case in which more than one interaction was found significant was handled by calculating composite mean squares and degrees of freedom according to the procedure described by Johnson and Keeping (33).

TABLE VI

BREAKDOWN OF VARIANCE

Source of Variance	Degrees of Freedom	Expectation of the Mean Square	Mean Square
A	3	$\sigma^2 + 2\sigma_{AB}^2 + 3\sigma_{AS}^2 + 6\sigma_A^2$	M_A
B	2	$\sigma^2 + 2\sigma_{AB}^2 + 4\sigma_{BS}^2 + 8\sigma_B^2$	M_B
S	1	$\sigma^2 + 3\sigma_{AS}^2 + 4\sigma_{BS}^2 + 12\sigma_S^2$	M_S
AxB	6	$\sigma^2 + 2\sigma_{AB}^2$	M_{AB}
AxS	3	$\sigma^2 + 3\sigma_{AS}^2$	M_{AS}
BxS	2	$\sigma^2 + 4\sigma_{BS}^2$	M_{BS}
Residual	6	σ^2	M_R
Total	23		

EXPERIMENTAL COOKS

The series of twenty-four cooks was placed in a random sequence and carried out according to the general pulping methods already described. The fixed cooking conditions and white liquor charge are given in Table VII. Five preliminary cooks were made in a five-pound rotary autoclave to obtain black liquors for recycling in the main series. Conditions for the preliminary cooks varied from the standard procedure only as shown in Table VIII. The residual effective alkali, residual sulfide, and organic solids in the five black liquors were determined. By solving the necessary simultaneous equations it was possible to obtain mixtures of two or three of these black liquors which would contain the levels of residual effective alkali and organic solids indicated in Table IX. The two levels of residual sulfide were attained by adding the required amount of sodium sulfide with the white liquor. The amount of sodium hydroxide used to prepare the white liquor was diminished by the extent necessary to compensate for the effective alkali contained in the added sodium sulfide. The results of the analyses on the preliminary cook black liquors and the make-up of the recycled black liquor mixtures are given in Tables XXXVI and XXXVII of the Appendix.

TABLE VII

COOKING CONDITIONS

White liquor charge	
Active alkali (as NaOH), %	17.0
Sulfidity $Na_2S/NaOH + Na_2S$ (as NaOH), %	25.0
Liquor ratio, ml./g.	5½/1
Maximum temperature, °C.	173
Time to maximum temperature, hr.	2
Time at maximum temperature, hr.	2

TABLE VIII

CHANGES IN CONDITIONS FOR PRELIMINARY COOKS

Cook	Active Alkali, %	Sulfidity, %	Time at Maximum Temperature, hr.
P 1	22	20.5	1
P 2	20	22.5	1.5
P 3	18	25.0	2
P 4	17	26.5	2.5
P 5	17	26.5	3

TABLE IX

FACTOR LEVELS OF BLACK LIQUOR VARIABLES

	Residual Alkali (Effective Alkali)		Organic Solids	Residual Sulfide (Na_2S as NaOH)	
Level	On the Basis of Wood, %	On the Basis of White Liquor Effective Alkali, %	On Wood, %	On the Basis of Wood, %	On the Basis of White Liquor Sodium Sulfide, %
1	0.44	3.0	13.3	1.11	26.1
2	0.74	5.0	16.6	2.22	52.1
3	1.03	6.9	19.9		
4	1.33	8.9			

PULP EVALUATION

As already stated five pulp properties were considered as the dependent variable measuring the effect of the recycled liquor on the pulping process. The total yield, lignin content, and alpha-cellulose content of the pulps were used because these properties should show variation if the recycled black liquor has an effect upon the completeness of cooking or upon the relative rates of the various pulping reactions. The permanganate number and brightness of the pulps were studied because of the practical importance of these properties.

The brightness of the pulps was measured on handsheets formed according to the regular brightness determination procedure (Institute Method 412). A spectral-reflectance curve prepared for one of the pulps with a General Electric Recording Spectrophotometer indicated that the reflectance was a nearly linear function of wavelength. Reflectance measurements were then made on all the pulps with a General Electric Reflectance Meter using three filters which passed effective wavelengths of 457, 542, and 631 mmu. These readings indicated that this appreciably straight-line condition was not deviated from and that any differences in the appearances of the pulps were differences in brightness and not chromaticity.

The reflectance measurement made at 542 mmu (either of the other wavelengths would have served equally as well) was taken as an indication of brightness and considered in the analysis of variance computation. The reflectance data for all three wavelengths are given in Table XXXIX of the Appendix. All reflectance values were determined between six

and eight days after cooking. Preliminary work showed there were no changes in the reflectance over this three-day period.

In addition to the twenty-four cooks made with recycled black liquor two all-white-liquor cooks were made. In the first cook (Cook 25) the fixed white liquor charge employed in the factorial series was used; in the second (Cook 26) this charge was increased by an amount equivalent to the residual chemical in the black liquor at levels a_4 and s_1. The purpose of these cooks was to indicate the changes that occur in the dependent variables over the alkali concentration range encountered in the factorial experiment.

RESULTS

EFFECT OF RECOOKING ON BLACK LIQUOR COMPONENTS

PULP AND BLACK LIQUORS PROPERTIES

The results of the analyses on the pulp and black liquors formed in the three experimental cooks are presented in Table X. The corrected black liquor volumes are calculations of the total volume of black liquor resulting from each cook. In the case of Cook A, it was found that the strong black liquor contained 71.2% of the total solids removed by the end of the fourth washing. The correction was made assuming that the volume of strong black liquor recovered represented the same percentage of the total black liquor volume. Calculations of the corrected black liquor volumes made it possible to express the results of the various black liquor analyses in absolute terms or in terms based on the wood used in the initial cook.

CHEMICAL CONSUMPTION CALCULATIONS

Table XI gives the amounts of cooking chemicals charged to each cook, and the amounts analytically found in the liquors at the start and completion of each cook. The effective alkali, sodium sulfide, and sodium hydroxide are reported as the total number of grams involved. Some of the pulping chemicals appeared to be consumed when the black liquor was recooked. The amounts involved, however, were small in comparison to the amounts consumed when cooking wood.

TABLE X

PULP AND BLACK LIQUOR PROPERTIES

Cook	A	B	C
Pulp properties			
Unscreened yield on wood, %	44.8	none	none
Permanganate number	27.0	--	--
Lignin on pulp, %	4.8	--	--
Alpha-cellulose on pulp, %	79.5	--	--
Pulp washing data			
Distribution of black liquor total solids, %			
Strong black liquor	71.2	--	--
Wash solution 1	20.0	--	--
2	6.5	--	--
3	1.5	--	--
4	0.8	--	--
Black liquor properties			
Corrected black liquor vol., ml.	2360[1]	2276[2]	1525[2]
Residual chemicals, g./l. as NaOH			
Effective alkali	4.88	32.81	52.03
Sodium sulfide	6.72	10.04	15.88

[1] Corrected on the basis of the solids found in the wash solutions.

[2] Corrected for a sample removed at the start of the cook.

TABLE XI

COOKING CHEMICAL CONTENT OF LIQUORS

Cook	Chemical	Start of Cook	Completion of Cook
A	Effective alkali, g.		
	White liquor	71.11	--
	Black liquor	--	11.53
	Sodium sulfide, g.		
	White liquor	20.32	--
	Black liquor	--	15.86
	Sodium hydroxide, g.		
	White liquor	60.95	--
	Black liquor	--	3.60
	Sulfidity, %	25.0	81.5
B	Effective alkali, g.		
	White liquor	71.11	--
	Black liquor	4.04	71.68
		75.15 (76.67)[1]	
	Sodium sulfide, g.		
	White liquor	20.32	--
	Black liquor	5.56	22.85
		25.88 (24.93)[1]	
	Sodium hydroxide, g.		
	White liquor	60.95	--
	Black liquor	1.26	60.25
		62.21	
	Sulfidity, %	29.4	27.5
C	Effective alkali, g.		
	White liquor	45.36	--
	Black liquor	47.90	79.15
		93.26 (87.47)[1]	
	Sodium sulfide, g.		
	White liquor	12.96	--
	Black liquor	14.66	24.15
		27.62 (24.66)[1]	
	Sodium hydroxide, g.		
	White liquor	38.88	--
	Black liquor	40.57	67.07
		79.45	
	Sulfidity, %	25.8	26.5

[1] Chemical found analytically in mixed liquor.

BLACK LIQUOR EVALUATION

Lignin Materials

The effect of recooking on the various lignin materials, including the phenolic fraction of the acid-precipitated, ether-soluble material, is shown in Table XII. The separations and analyses were made on duplicate samples of the three black liquors. Some degradation of the acid-precipitated, ether-insoluble lignin is indicated by the decreased yields of this fraction, and by the increased combined yields of the ether-soluble and the acid-soluble fractions. The extent of degradation, approximately a 7% loss per cook, is similar to that found by Kimble (15) on recooking an isolated thiolignin. No appreciable change in the methoxyl content or the ethanol solubility of this material appears to take place.

The good agreement between the totals of the three lignin fractions and the somewhat inconsistent distributions between the ether-soluble and acid-soluble lignins may indicate differences in the conditions under which the acid-insoluble materials were precipitated. There were appreciable differences between the amounts of inorganic materials present in the three black liquors.

The ultraviolet absorption curves for the solutions of the acid-soluble fractions from the three cooks were similar. This curve for the solution from Cook A and the curve for an isolated native lignin are included in Figure 2.

TABLE XII

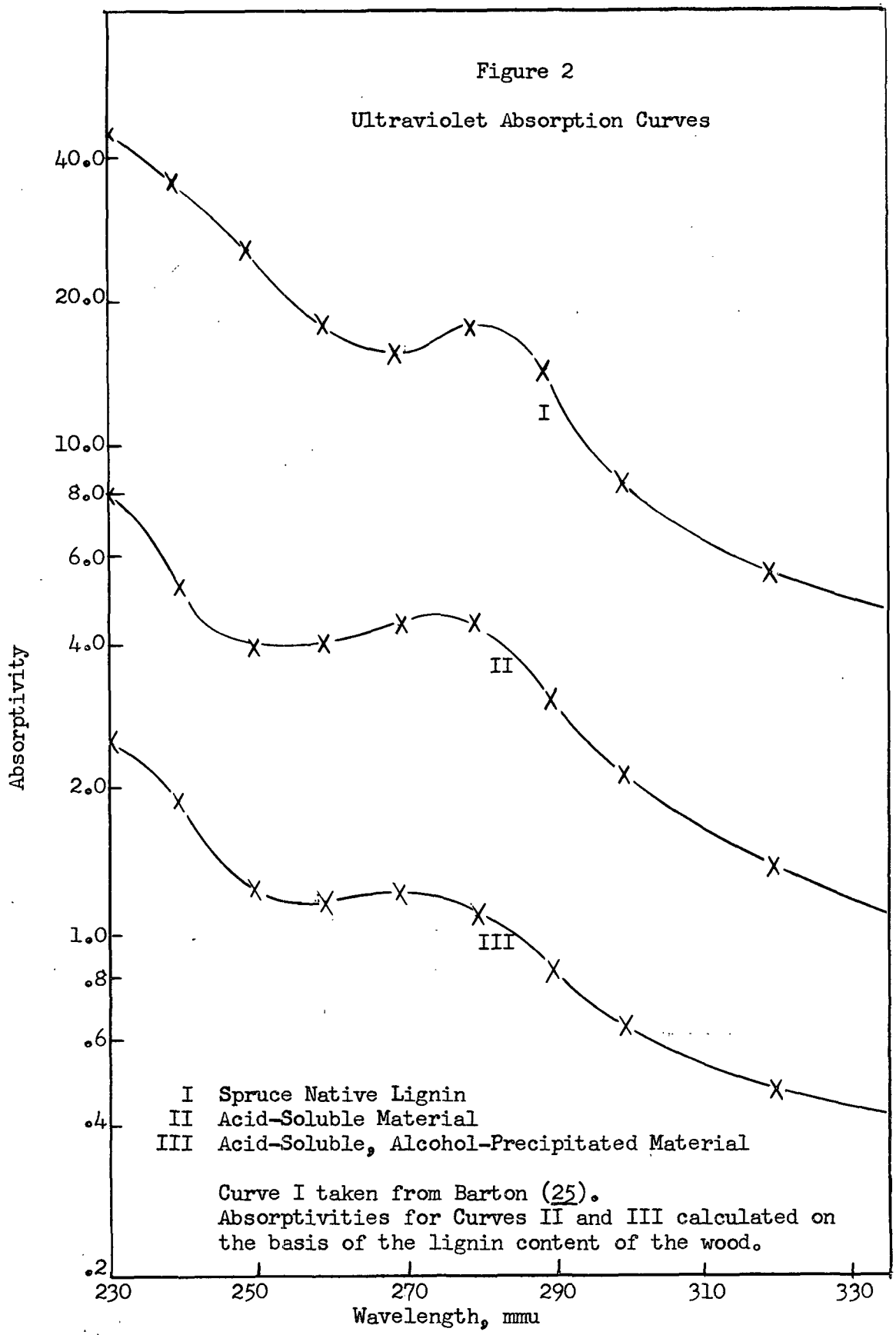
EFFECT OF RECOOKING ON THE LIGNIN MATERIALS

Black liquor	Cook A	Cook B	Cook C
Acid-precipitated, ether-insoluble lignin			
Yield/100 g. wood			
Sample 1	15.26	14.22	12.31
Sample 2	14.69	13.65	12.91
Average	14.98	13.94	12.61
Methoxyl content, %[1]			
Sample 1	13.54	13.96	12.73
Sample 2	13.54	13.50	13.86
Average	13.54	13.73	13.30
Ethanol insolubility, %			
Sample 1	68.5	71.4	61.2
Sample 2	70.3	72.9	58.1
Average	69.4	72.2	59.7
Acid-precipitated, ether-soluble, phenolic material			
Yield/100 g. wood			
Sample 1	3.24	2.11	6.26
Sample 2	3.29	4.41	7.96
Average	3.26	3.26	7.11
Acid-soluble lignin (by ultraviolet absorption)			
g. lignin/100 g. wood			
Measured at 220 mmu	5.22	7.04	5.25
Measured at 280 mmu	6.32	7.18	5.25
Average	5.77	7.11	5.25

[1] Reported methoxyl values are averages from duplicate determinations.

Figure 2

Ultraviolet Absorption Curves



I Spruce Native Lignin
II Acid-Soluble Material
III Acid-Soluble, Alcohol-Precipitated Material

Curve I taken from Barton (25).
Absorptivities for Curves II and III calculated on the basis of the lignin content of the wood.

Acid-Precipitated, Ether-Soluble Material

Table XIII gives the results of the separations of the ether-dioxane (40:1) soluble materials into acidic, phenolic, and neutral fractions. The poor reproducibility obtained was probably caused, in part, by the following factors: (a) the indirect method of determination, (b) the volatility of the materials, and (c) the relatively large amounts of free sulfur and possibly other incidental materials included with the neutral fraction.

The phenolic fraction has been considered as a lignin product and discussed elsewhere. No consistent change in the acidic fraction on recooking is indicated.

TABLE XIII

EFFECT OF RECOOKING ON THE
ACID-PRECIPITATED, ETHER-SOLUBLE MATERIALS

Black liquor	Cook A	Cook B	Cook C
Acid-precipitated, ether-soluble material g. yield/100 g. wood			
Phenolic material			
Sample 1	3.24	2.11	6.26
Sample 2	3.29	4.41	7.96
Average	3.26	3.26	7.11
Acidic material			
Sample 1	3.48	4.27	5.75
Sample 2	3.04	6.11	3.18
Average	3.26	5.19	4.47
Neutral material			
Sample 1	0.83	2.67	2.07
Sample 2	1.45	0.91	6.44

Acid-Soluble, Alcohol-Precipitated Material

The results of the analyses on the acid-soluble, alcohol-precipitated material are given in Table XIV and indicate that the small amount of this material found in the black liquor is only slowly destroyed on recooking. Qualitative paper partition chromatograms disclosed that upon hydrolysis this material yielded xylose, arabinose, and galactose and that the precursors of none of those sugars appeared to be preferentially destroyed on recooking. These results are in agreement with the results of a study recently published by Saarnio and Gustafsson (34) in which a paper partition chromatography technique was used to show that in the sulfate pulping of pine the dissolved glucan and mannan are rapidly destroyed, but the dissolved xylan, araban, and galactan are more resistant and remain in the cooking liquor for some time.

The small amounts of ligneous material found had ultraviolet absorption curves which are different from those obtained with native lignins or with the total acid-soluble fraction. The curve found in the case of Cook A is included in Figure 2. The shape of the curves was similar to that reported by Enkvist and Alfredsson (35) for a low methoxyl lignin degradation product which is formed at about 100°C. during the early part of an ordinary sulfate cook.

TABLE XIV

EFFECT OF RECOOKING ON THE
ACID-SOLUBLE, ALCOHOL-PRECIPITATED MATERIAL

Black liquor	A	B	C
Reducing value Expressed as g. glucose/100 g. wood			
Nonhydrolyzed	Negligible	Negligible	Negligible
Hydrolyzed			
Sample 1	1.10	0.63	0.45
Sample 2	0.94	0.69	0.57
Average	1.02	0.66	0.51
Component sugars (by paper partition chromatography)			
Predominant sugars	Xylose Arabinose Galactose		Xylose Arabinose Galactose
Trace sugars	Glucose Mannose		Glucose Mannose
Ultraviolet absorption Expressed as g. lignin/100 g. wood			
Measured at 220 mmu	0.16	0.24	0.32
Measured at 280 mmu	0.16	0.22	0.24
Average	0.16	0.23	0.28

Volatile Acids

The data for the volatile acid determinations are given in Table XV. A small increase in volatile acids is indicated and appears to arise from a degradative reaction which is largely completed during the first recook. The relatively large amounts of acid found in the final condensate fractions point out the empirical nature of this method.

TABLE XV

EFFECT OF RECOOKING ON THE VOLATILE ACIDS

Black liquor	Cook A		Cook B		Cook C	
Condensate fractions						
Meq. acids in condensate fractions of duplicate runs						
Fraction 1	0.154	0.156	0.132	0.138	0.193	0.204
2	0.107	0.113	0.087	0.094	0.147	0.148
3	0.077	0.087	0.063	0.050	0.080	0.081
4	0.056	0.052	0.041	0.036	0.053	0.045
5	0.041	0.031	0.028	0.030	0.032	0.031
Total	0.435	0.439	0.351	0.348	0.505	0.509
Volatile acids						
Meq./100 g. wood						
Sample 1	91.0		100.9		101.0	
Sample 2	91.6		100.0		101.9	
Average	91.3		100.5		101.5	
g. acetic acid/100 g. wood	5.48		6.03		6.09	

Acid-Soluble, Alcohol-Soluble, Nonvolatile Acids

The results of the analyses on the acid-soluble, alcohol-soluble, nonvolatile acids are presented in Table XVI. The data in no instance indicate that the recooking brings on any appreciable changes in the components of this fraction.

TABLE XVI

EFFECT OF RECOOKING ON THE
ACID-SOLUBLE, ALCOHOL-SOLUBLE, NONVOLATILE ACIDS

Black liquor	Cook A	Cook B	Cook C
Acidity determinations			
ml. eq./100 g. wood			
Free acids	97.2	106.0	104.6
Saponification value	31.0	41.8	31.2
Gravimetric determination			
g./100 g. wood			
Total acidic fraction (corrected for non-acidic residues)	17.91	21.05	18.42
Fractionation			
Summation of fractions			
Acidity, ml. eq./100 g. wood			
Sample 1	76.6	75.4	90.5
Sample 2	83.8	81.6	95.8
Average	80.2	78.5	93.1
Weight, g./100 g. wood			
Sample 1	7.41	6.35	7.25
Sample 2	7.13	6.84	7.28
Average	7.27	6.60	7.26
Average equivalent weight	91	84	78
Free acids included in the fractionation, %	83	74	89

Although these acid materials are probably primarily of carbohydrate origin, some acid-soluble lignin residues are undoubtedly being included in the determinations of the saponification value and the total weight of the fraction. Ultraviolet absorption measurements, made on another sample of the acid-soluble solution before and after the same neutralization and exchange resin treatments, indicated that approximately two-thirds of the original soluble lignin was still present in this fraction. The fact that the soluble lignin content was highest in the

black liquor from Cook B might explain the generally higher results obtained for this liquor in these determinations.

The results of the fractionation experiments indicate that recooking causes little, if any, change in the equivalent weight distributions of the major portion of these acidic materials. In Figure 3 the average equivalent weights of these fractions are plotted against the equivalents of acid eluted from the exchange-resin column. The data from fractionations on duplicate samples were used to obtain the curve for each cook.

Acid-Soluble, Alcohol-Soluble, Neutral Residues

Table XVII lists the results of the determinations of the acid-soluble, alcohol-soluble, neutral residues. The amount of this material occurring in the black liquor is not large, and it is not greatly affected by recooking.

The negative results of the tests for ultraviolet absorption and for reducing value suggest that this fraction consists primarily of nonaromatic material which may consist of lignin degradation products similar to those described by Enkvist and Alfredsson (35).

Summary of Black Liquor Evaluation

A summary of the effect of recooking on the black liquor components is given in Table XVIII.

Figure 3

Fractionation of Acid-Soluble Acids

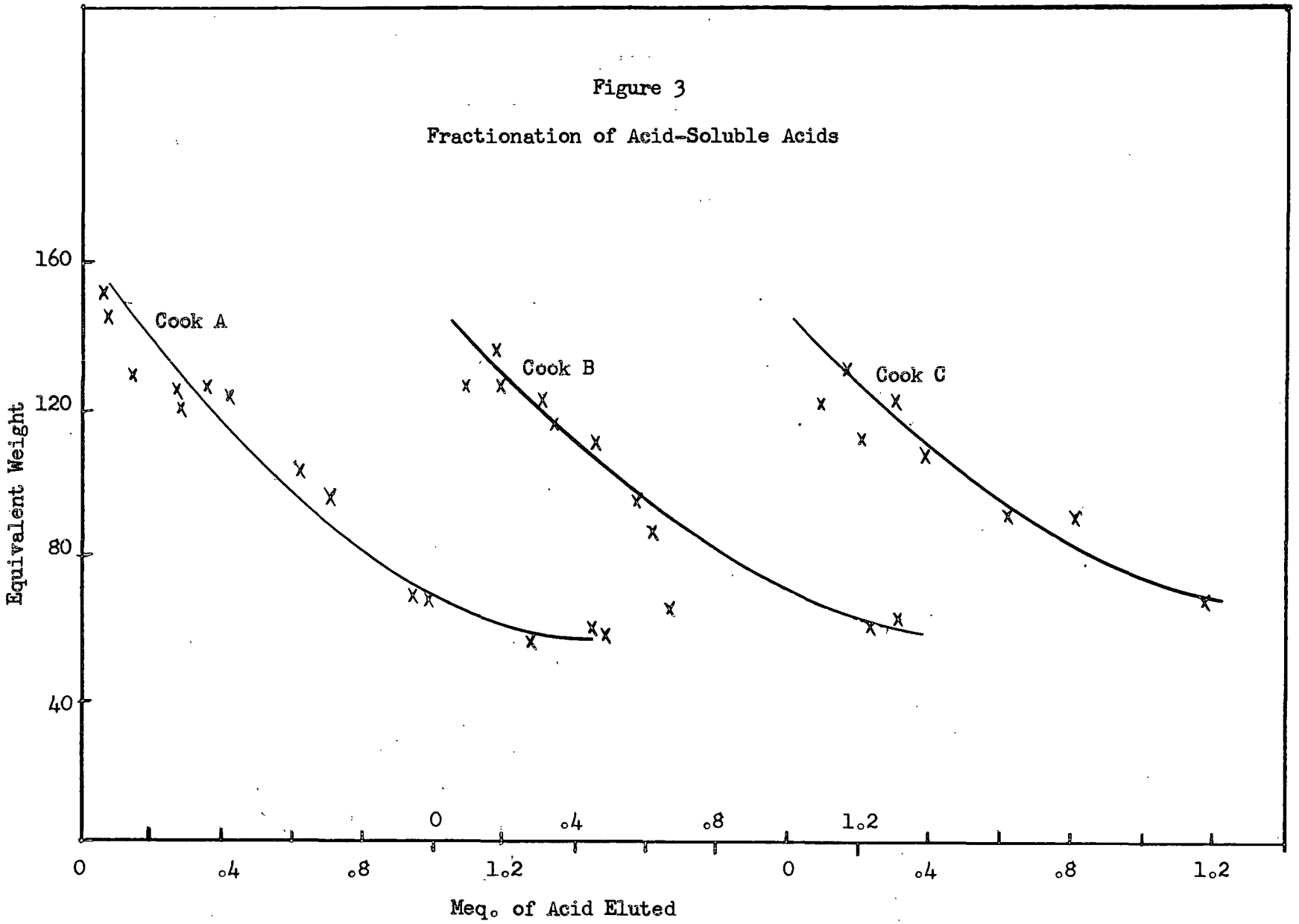


TABLE XVII

EFFECT OF RECOOKING ON ACID-SOLUBLE, NEUTRAL RESIDUES

Black liquor	Cook A	Cook B	Cook C
Weight			
g./100 g. wood			
Sample 1	1.41	1.40	1.68
Sample 2	1.42	1.43	1.71
Average	1.42	1.42	1.70
Reducing value			
as g. glucose/100 g. wood			
Nonhydrolyzed	Negligible	Negligible	Negligible
Hydrolyzed	0.124	0.080	0.084
Ultraviolet absorption	Negligible	Negligible	Negligible

TABLE XVIII

EFFECT OF RECOOKING ON THE CONSTITUENTS OF SULFATE BLACK LIQUOR

Grams of material per 100 grams of wood.

Fraction	Cook A	Cook B	Cook C
Lignin			
Acid and ether insoluble	14.98	13.94	12.61
Acid-insoluble, ether-soluble	3.26	3.26	7.11
Acid-soluble	5.77	7.11	5.25
	24.01	24.31	24.97
Acid-insoluble acids	3.26	5.19	4.47
Alcohol-insoluble, carbohydrates (reducing value calculated as glucose)	1.02	0.66	0.51
Volatile acids (as acetic)	5.48	6.03	6.09
Acid-soluble, nonvolatile, acids	17.91	21.05	18.42
(meq. free acids)	(97.2)	(106.0)	(104.6)
Acid-soluble, neutral residue	1.42	1.42	1.70
Total material	53.10	58.66	56.16

EFFECT OF THE PROPERTIES OF RECYCLED BLACK LIQUOR ON PULPING

The results of the factorially designed pulping study are given in the following tables. In Tables XIX through XXIII the results of the analyses for the various dependent variables are presented. The values given for the lignin content, alpha-cellulose content, and permanganate number are the averages for duplicate determinations. The brightness values are averages for three or five measurements.

Table XXIV lists for each dependent variable, the mean square attributable to each source of variance. A more complete summarization of the analysis of variance calculations is given in Table XXVIII of the Appendix.

The analysis of variance indicates that of the factors considered, only the residual effective alkali affects the total yield of pulp obtained. Using the results found at the various levels of the other two factors, the average yield for each of the four residual effective alkali levels was calculated. These averages are listed in Table XXV, and they show that the residual effective alkali in the recycled liquor decreases the yield of pulp obtained.

In considering the effect of the recycled black liquor properties on the lignin content of the pulp, the data indicate that the three interaction terms, and particularly the BxS interaction, are significant. The meaning of a significant interaction effect is best seen by rearranging the data into the appropriate two-factor table. Each term of the BxS table, for example, is obtained by averaging the values of the dependent variable found at the four levels of A.

TABLE XIX

TOTAL YIELD
(On Wood, %)

Residual Sulfide on Wood, %	Organic Material on Wood, %		Residual Effective Alkali on Wood, %			
			a_1	a_2	a_3	a_4
			0.44	0.74	1.03	1.33
s_1	b_1	13.3	45.6	45.2	46.5	43.9
1.11	b_2	16.6	46.5	45.6	44.6	46.5
	b_3	19.9	46.7	47.4	43.6	47.0
s_2	b_1	13.3	46.1	45.8	44.3	45.4
2.22	b_2	16.6	48.3	45.2	45.2	43.6
	b_3	19.9	47.2	45.6	45.6	44.3

TABLE XX

LIGNIN CONTENT
(Of Pulp, %)

Residual Sulfide on Wood, %	Organic Material on Wood, %		Residual Effective Alkali on Wood, %			
			a_1	a_2	a_3	a_4
			0.44	0.74	1.03	1.33
s_1	b_1	13.3	6.7	7.0	7.4	6.6
1.11	b_2	16.6	8.1	6.7	7.0	5.9
	b_3	19.9	9.3	7.8	8.5	8.6
s_2	b_1	13.3	7.7	7.5	7.1	5.9
2.22	b_2	16.6	8.0	6.7	5.8	5.4
	b_3	19.9	8.2	6.6	5.3	6.8

TABLE XXI

ALPHA-CELLULOSE CONTENT
(Of Pulp, %)

Residual Sulfide on Wood, %	Organic Material on Wood, %		Residual Effective Alkali on Wood, %			
			a_1	a_2	a_3	a_4
			0.44	0.74	1.03	1.33
s_1	b_1	13.3	76.9	76.5	77.5	77.6
1.11	b_2	16.6	75.6	77.3	76.6	75.8
	b_3	19.9	73.3	75.3	74.9	75.4
s_2	b_1	13.3	74.6	75.6	78.1	76.5
2.22	b_2	16.6	75.5	75.4	78.1	76.7
	b_3	19.9	74.5	75.3	76.3	76.9

TABLE XXII

PERMANGANATE NUMBERS

Residual Sulfide on Wood, %	Organic Material on Wood, %		Residual Effective Alkali on Wood, %			
			a_1	a_2	a_3	a_4
			0.44	0.74	1.03	1.33
s_1	b_1	13.3	29.5	29.5	28.6	30.0
1.11	b_2	16.6	31.2	28.7	29.5	27.6
	b_3	19.9	32.0	30.6	30.6	31.1
s_2	b_1	13.3	29.7	29.1	25.9	27.7
2.22	b_2	16.6	30.6	28.6	25.7	26.9
	b_3	19.9	30.0	28.5	28.2	28.4

TABLE XXIII

BRIGHTNESS
(Reflectance at 542 mmu, %)

Residual Sulfide on Wood, %	Organic Material on Wood, %		Residual Effective Alkali on Wood, %			
			a_1	a_2	a_3	a_4
			0.44	0.74	1.03	1.33
s_1	b_1	13.3	27.6	29.3	28.2	29.5
1.11	b_2	16.6	27.1	29.9	29.9	30.3
	b_3	19.9	25.2	26.7	26.0	26.5
s_2	b_1	13.3	29.2	28.8	31.0	31.5
2.22	b_2	16.6	26.8	28.6	32.0	31.4
	b_3	19.9	25.8	28.9	29.1	28.7

TABLE XXIV

RESULTS OF THE ANALYSIS OF VARIANCE CALCULATIONS

Source of Variance	Total Yield on Wood, %	Lignin Content on Pulp, %	Alpha-Cellulose Content on Pulp, %	$KMnO_4$ Number	Brightness
A	390[1]	239	384[3]	646[3]	881[3]
B	67	185	454	421[1]	1452[3]
S	26	308	3	1601[3]	1014[3]
AxB	77	71[1]	43	110	87
AxS	143	73[1]	128	157	195
BxS	18	201[2]	190[1]	67	137
Residual	202	9	38	46	54

[1] Significant at the 5% level.

[2] Significant at the 1% level.

[3] Significant at the 0.1% level.

TABLE XXV

AVERAGE TOTAL YIELDS

Residual Effective Alkali Level	Total Yield on Wood, %
a_1	46.7
a_2	45.8
a_3	45.0
a_4	45.1

The two-factor tables for the lignin contents of the pulps are given as Tables XXVI to XXVIII. At the lower sulfide level the lignin content increased when the amount of recycled organic material was increased. At the higher sulfide level this effect did not take place. The residual effective alkali reduced the lignin content of the pulps, and this reduction was more pronounced at the higher sulfide level and at the lower recycled organic material levels.

The results of the analysis of variance on the alpha-cellulose content can be interpreted in two ways. The actual implications are, in either case, quite similar. The BxS interaction is just significant at the 5% level; the AxS interaction is not significant but is suspiciously large. Under these circumstances the arbitrary procedure of accepting one interaction and rejecting the other does not appear justified. If both are accepted the main effects are found to be nonsignificant at the 5% level; if both are rejected the A and B main effects are both found to be significant at the 0.1% level.

TABLE XXVI

LIGNIN CONTENT
AxB TWO-FACTOR TABLE
(On Pulp, %)

Organic Material Level	Residual Effective Alkali Level			
	a_1	a_2	a_3	a_4
b_1	7.2	7.3	7.3	6.8
b_2	8.1	6.7	6.4	5.7
b_3	8.8	7.2	6.9	7.9

TABLE XXVII

LIGNIN CONTENT
AxS TWO-FACTOR TABLE
(On Pulp, %)

Residual Sulfide Level	Residual Effective Alkali Level			
	a_1	a_2	a_3	a_4
s_1	8.0	7.2	7.6	7.0
s_2	8.0	6.9	6.1	6.0

TABLE XXVIII

LIGNIN CONTENT
BxS TWO-FACTOR TABLE
(On Pulp, %)

Residual Sulfide Level	Organic Material Level		
	b_1	b_2	b_3
s_1	6.9	6.9	8.6
s_2	7.1	6.5	6.7

A reasonable conclusion appears to be that the alpha-cellulose content of the pulp is affected by both the residual effective alkali and the organic material in the recycled black liquor, and that the effects of these factors are probably influenced by the residual sulfide level. The two-factor tables, Tables XXIX and XXX, indicate that the organic material reduces the alpha-cellulose content, particularly at the lower sulfide level, and that the effective alkali increases the alpha-cellulose content, particularly at the higher sulfide level.

Two additional sets of analyses of variance calculations were made using data in which the alpha-cellulose and lignin determination results were expressed on the basis of the wood instead of the pulp. No significant effects were found for the alpha-cellulose data. In the case of the lignin results the three interaction terms were again found to be significant. The results of these calculations are included in Table XXXVIII of the Appendix.

The analyses of variance for the data on the permanganate number and the brightness of the pulp indicate that both of these properties are significantly affected by the three main effects. Average values calculated for these pulp properties at the various levels of the three factors are given in Tables XXXI and XXXII. The tables show that the residual effective alkali and the residual sulfide cause a lower permanganate number and higher brightness, but at the same time the recycled organic material exerts the opposite effect on both of these properties.

TABLE XXIX

ALPHA-CELLULOSE
AxS TWO-FACTOR TABLE
(On Pulp, %)

Residual Sulfide Level	Residual Effective Alkali Level			
	a_1	a_2	a_3	a_4
s_1	75.3	76.4	76.3	76.3
s_2	74.9	75.4	77.5	77.0

TABLE XXX

ALPHA-CELLULOSE
BxS TWO-FACTOR TABLE
(On Pulp, %)

Residual Sulfide Level	Organic Material Level		
	b_1	b_2	b_3
s_1	77.1	76.3	74.7
s_2	76.2	76.4	75.8

TABLE XXXI

AVERAGE PERMANGANATE NUMBERS

Residual Effective Alkali Levels	$KMnO_4$ No.	Organic Material Levels	$KMnO_4$ No.	Residual Sulfide Levels	$KMnO_4$ No.
a_1	30.5	b_1	28.9	s_1	30.0
a_2	29.2	b_2	28.6	s_2	28.3
a_3	28.1	b_3	29.9		
a_4	28.8				

TABLE XXXII

AVERAGE BRIGHTNESS VALUES
(Reflectance at 542 mmu, %)

Residual Effective Alkali Levels	Brightness, %	Organic Material Levels	Brightness, %	Residual Sulfide Levels	Brightness, %
a_1	27.0	b_1	29.4	s_1	28.0
a_2	28.7	b_2	29.5	s_2	29.3
a_3	29.4	b_3	27.1		
a_4	29.7				

TABLE XXXIII

PROPERTIES OF PULPS MADE WITH WHITE LIQUOR ALONE

Cook		25	26
Unscreened yield, %		47.4	43.6
Alpha-cellulose, %		72.8	80.0
Lignin, %		9.2	5.4
Permanganate number		30.4	25.6
Reflectance, %			
Filter	1	19.5	23.5
	5	27.2	32.0
	8	37.9	42.9

In Table XXXIII the results of the analyses made on the pulps of the two all-white-liquor cooks are given. The data point out the fact that the amounts of residual effective alkali considered in the factorial experiment were such that if similar changes were made in the white liquor charge, the pulp properties would be appreciably affected. A comparison of the yields in these cooks with the average pulp yield for the a_4 level of residual effective alkali (45.1%)

suggests that the cooking value of the residual effective alkali indicated by the analytical method used is somewhat less than that of a similar amount of white liquor effective alkali.

SUMMARY OF FACTORIAL EXPERIMENT RESULTS

A summary of the effect of the residual effective alkali, organic material, and residual sulfide contents of the recycled black liquor on the pulp properties is given in Table XXXIV.

TABLE XXXIV

SUMMARY OF FACTORIAL EXPERIMENT RESULTS

Dependent Variable	Main Effects and Significant Interactions	Mode of Action (Effect of increasing level of factor)
Yield	A	Decreases yield
	B	None
	S	None
Lignin content	AxB	Effect of each factor dependent upon levels of other two factors.
	AxS	
	BxS	
Alpha-cellulose content	AxS	Effect of A and B dependent upon level of S.
	BxS	
Permanganate number	A	Decreases permanganate no.
	B	Increases permanganate no.
	S	Decreases permanganate no.
Brightness	A	Increases brightness
	B	Decreases brightness
	S	Increases brightness

A Residual effective alkali

B Organic material

S Residual sulfide

SUMMARY

An investigation was conducted which has contributed to an understanding of the role of recycled black liquor in the sulfate pulping process. The pulping of jack pine was studied using cooking conditions which gave yields of about 45%.

Because of the possibility that the organic residues in the recycled liquor might react further and decrease the amount of pulping chemicals available to the wood, the possible degradation of these residues on recooking was investigated. A black liquor prepared in an initial cook with wood was recooked twice with fresh quantities of white liquor but in the absence of wood. The original black liquor and the two recooked liquors were compared by being subjected to a scheme of analyses which involved the separation and characterization of the various groups of components present in black liquor.

To determine if the sulfate pulping process is affected by the residual effective alkali, the residual sulfide, or the organic material in the recycled black liquor, a series of cooks was made in which these properties of the recycled liquor were varied according to a factorial design pattern. The desired levels of the properties were obtained by using mixtures of black liquors prepared in preliminary laboratory cooks and by adding to these mixtures the necessary amounts of fresh sodium sulfide.

The effect these properties of the recycled black liquor had on the pulping process was measured in terms of the effect on the total yield, lignin content, alpha-cellulose content, permanganate number, and brightness of the pulps. The statistical method of analysis of variance was employed to determine if the properties of the recycled black liquor had significant effects on the pulping process.

CONCLUSIONS

The following conclusions can be made concerning the role of recycled black liquor in the sulfate pulping situation studied.

1. The organic material in the recycled black liquor is relatively resistant to degradative changes during recooking. The following results were obtained on recooking black liquor with white liquor in the absence of wood. Because of the continuing high alkali concentration under such recooking conditions, these results probably indicate greater changes then would have been encountered if the black liquor had been recooked along with a fresh charge of wood.

(a) Some degradation of the larger lignin residues is shown by the small decrease (7% per cook) in the amount of acid-precipitated, ether-soluble lignin which was recovered.

(b) The small amount (1% of the wood) of polysaccharides present in the initial black liquor was only slowly destroyed on recooking. This material contained a mixture of xylans, arabans, and galactans and underwent only a 34% decrease during the first recooking treatment.

(c) The amount of volatile acids in the black liquor increased slightly (less than 10%) during the first recook. There was little additional increase on further recooking.

(d) The acidic reaction products derived from the carbohydrate portion of the wood do not appear to have undergone significant changes in either total amount or in equivalent weight.

2. On the basis of the relative stability of the black liquor, and the fact that the changes which do occur involve primarily components present in small amounts or components whose alkali consumption is not high (36), it appears that the recooking of black liquor could not effect an appreciable consumption of cooking chemical. This is in agreement with the results of the analytical determinations for residual chemicals in the black liquors. It can be concluded, therefore, that any effects which recycled black liquor has on the pulping process cannot be explained on the basis of an appreciable consumption of white liquor chemicals by the organic constituents of the recycled black liquor. This conclusion is supported by the results of the factorial experiment in which it was shown that the pulp yield is affected by the amount of alkali in the cooking liquor but is not affected by the amount of recycled organic material present.

3. The residual effective alkali occurring in the recycled black liquor has actual value as a cooking agent. This is indicated by its effect upon the yield, lignin content, alpha-cellulose content, permanganate number, and brightness of the pulp. On the basis of the limited evidence afforded by a comparison between the factorial series cooks and two all-white-liquor cooks, it would appear that the cooking value of the residual effective alkali indicated by TAPPI Standard T 625 m-48 (potentiometric titration to pH 8.3 after treatment with barium chloride) is only somewhat less than that of the same amount of white liquor alkali.

4. Although the recooking of the organic material in recycled black liquor does not appear to involve an appreciable consumption of

cooking chemicals, the presence of the organic material in the cooking liquor does affect the pulping process. The following effects on the pulp properties were indicated by the results of the factorial experiment.

(a) The recycled organic material increases the permanganate number and decreases the brightness of the pulp.

(b) The effect of this material on the lignin content of the pulp is dependent upon both the amount of residual alkali and residual sulfide in the recycled liquor. Only at a low sulfide or low alkali level, does the presence of the organic material result in pulps containing larger amounts of lignin.

(c) The alpha-cellulose content of the pulp is decreased by the organic material in the recycled liquor. This effect is minimized or overcome if the sulfide content of the recycled liquor is sufficiently high.

5. The residual sulfide content of the recycled black liquor also exerts an appreciable affect on the pulping process. This material, like the residual alkali, decreases the permanganate number and increases the brightness of the pulp. In addition significant interaction effects were found which indicate that the residual sulfide increases the effect of the residual alkali and decreases the effect of the recycled organic material on the lignin and alpha-cellulose contents of the pulps.

6. The factorial experiment has shown that the effect of a recycled black liquor on the pulping process is dependent upon the properties of the black liquor recycled. The residual chemicals and the organic materials in the recycled black liquor have been found to have opposing effects on several properties of the pulps.

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APPENDIX

TABLE XXXV

WOOD CHARACTERIZATION

	Stick 1	Stick 2	Stick 3	Combined Sample
Physical Examination				
Moisture, %[1]				39.8
Density, g./cc. (Ovendry wt. and vol.)	0.444	0.393	0.370	
Growth rate, rings/in.	7.02	8.54	7.17	
Diameter, average in.	5.12	6.44	7.25	
Chemical Analyses (basis, ovendry wood)				
Lignin, %				26.5
Alpha-cellulose, %[1]				39.7
Pentosans, %[1]				8.4
Extractives, %[1] (benzene-ethanol)				3.7

[1]Results of duplicate determinations averaged.

TABLE XXXVI

FACTORIAL EXPERIMENT
PROPERTIES OF PRELIMINARY COOK BLACK LIQUORS

Cook	Residual Effective Alkali g./l. as NaOH	Organic Solids, g./l.	Residual Sulfide, g./l. as NaOH
P 1	9.80	95.3	3.35
P 2	6.56	88.2	2.50
P 3	3.59	85.4	2.70
P 4	1.54	71.7	3.76
P 5	1.68	75.3	6.08

TABLE XXXVII

FACTORIAL EXPERIMENT
MAKE-UP OF RECYCLED BLACK LIQUORS

Cooks	Black Liquor Volumes in ml. P 1	P 2	P 3	P 4	P 5	Total Sulfide as g. NaOH
1 & 13	404	-	-	354	-	2.42
2 & 14	367	300	-	-	24	1.89
3 & 15	-	558	100	-	18	1.84
4 & 16	-	-	607	-	30	2.22
5 & 17	223	-	-	782	-	3.54
6 & 18	709	100	-	-	71	2.60
7 & 19	-	653	-	-	232	3.04
8 & 20	-	-	564	-	280	3.59
9 & 21	39	-	-	1209	-	4.65
10 & 22	785	-	-	-	304	3.97
11 & 23	-	580	-	-	518	4.60
12 & 24	-	-	520	-	536	5.00

TABLE XXXVIII

ANALYSIS OF VARIANCE RESULTS

Source of Variance	Degrees of Freedom	Total Yield on Wood, %		Permanganate Number		Brightness, %	
		Sums of Squares	Mean Squares	Sum of Squares	Mean Squares	Sum of Squares	Mean Squares
A	3	1169	390[1]	1939	646[2]	2643	881[3]
B	2	134	67	842	421[1]	2904	1452[3]
S	1	26	26	1601	1601[3]	1014	1014[2]
AxB	6	462	77	662	110	520	87
AxS	3	430	143	470	157	584	195
BxS	2	36	18	133	67	273	137
Residual	6	1214	202	273	46	324	54

Source of Variance	Lignin Content				Alpha-Cellulose Content			
	On Pulp, %		On Wood, %		On Pulp, %		On Wood, %	
	Sum of Squares	Mean Squares	Sum of Squares	Mean Squares	Sum of Squares	Mean Squares	Sum of Squares	Mean Squares
A	718	239	752	251	1153	384[3]	137	46
B	369	185	281	140	909	454	64	32
S	308	308[1]	338	338	3	3	26	26
AxB	426	71[1]	394	66[3]	258	43	565	94
AxS	219	73[1]	262	87[3]	384	128	275	92
BxS	402	201[2]	375	188[3]	381	190[1]	6	3
Residual	54	9	22	4	232	38	361	94

[1] Significant at 5% level
[2] Significant at 1% level
[3] Significant at 0.1% level

TABLE XXXIX

REFLECTANCE DATA FOR FACTORIAL EXPERIMENT PULPS

Cook	Reflectance, % Filter 1	Filter 5	Filter 8
1	20.2	27.6	37.7
2	21.4	29.3	40.4
3	20.6	28.2	38.4
4	21.5	29.5	40.1
5	19.6	27.1	38.2
6	21.8	29.9	41.0
7	22.1	29.9	41.6
8	22.0	30.3	40.6
9	18.6	25.2	35.9
10	19.5	26.7	37.7
11	18.4	26.0	34.5
12	19.0	26.5	37.3
13	21.3	29.2	40.1
14	21.1	28.8	38.6
15	23.2	31.0	42.5
16	23.1	31.5	41.6
17	19.3	26.8	37.8
18	20.7	28.6	39.8
19	22.2	32.0	41.9
20	22.9	31.4	42.7
21	18.6	25.8	36.3
22	21.0	28.9	39.3
23	21.5	29.1	39.6
24	20.9	28.7	39.1
25	19.5	27.2	37.9
26	23.5	32.0	42.9

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